

lization from methyl isobutyl ketone gave pure IV, m.p. 191.2–193.4° (corr.).

*Anal.* Calcd. for  $C_{25}H_{22}O_2S_2$ : C, 73.97; H, 4.87; S, 14.10. Found: C, 74.11; H, 4.74; S, 14.12; N, none.

IV is insoluble in water and ethanol, slightly soluble in acetone and methyl isobutyl ketone, and soluble in toluene.

IV was characterized by its saponification products, oxalic acid, and benzhydryl mercaptan obtained by refluxing 1.5 g. in ethanol (20 ml.) and 10% potassium hydroxide solution (10 ml.) for several hours. After acidification (to pH 2) of the mixture with 5% hydrochloric acid, oxalic acid was obtained by first separating the benzhydryl mercaptan as a benzene extract, then concentrating *in vacuo* the aqueous solution to about 5 ml., whereupon precipitation occurred. Oxalic acid was separated from salt in this precipitate by ether extraction. It was identified by m.p. (184°)<sup>15</sup> comparison of its infrared spectrum with that of authentic oxalic

(15) Lit.: 189.5°; E. Bamberger and M. Althausse, *Ber.*, 21, 1901 (1888).

acid, and determination of its neutralization equivalent: Calcd., 63.03; found, 63.96.

The presence of benzhydryl mercaptan in the saponification mixture was shown by its oxidation to dibenzhydryl disulfide, m.p. 150–152° (corr.).<sup>16</sup> In this case saponification was accomplished under nitrogen, and the reaction mixture then was made only weakly acidic (pH 5–6). The mercaptan was oxidized *in situ* to the disulfide by addition of a standard 1N iodine solution in the manner described by Biilman.<sup>16</sup>

IV was also characterized by fusion with benzylamine<sup>17</sup> to give *N,N'*-dibenzylamide, m.p. 218.5–221.1° (corr.).<sup>18</sup>

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(16) Lit.: 152°; E. Biilman, *Ann.*, 364, 328 (1907).

(17) The reaction conditions used were those developed by O. C. Dermer and J. King, *J. Org. Chem.*, 8, 171 (1943), for the preparation of *N*-benzylamide derivatives of unsubstituted amides.

(18) Lit.: 222–223°; cf. J. Strakosch, *Ber.*, 5, 694 (1872).

[CONTRIBUTION FROM THE ORGANIC PROCESS DEVELOPMENT DEPARTMENT, TEXAS DIVISION, DOW CHEMICAL CO.]

## Halogenation of Aldehydes. Chlorination of Propanal

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The chlorination of propanal in aqueous hydrochloric acid can be controlled in such a manner as to produce either 2-chloropropanal or 2,2-dichloropropanal in yields exceeding 85%. Previously unreported 2,2-dichloropropanal, 2,2-dichloropropanol, and 2,4,6-tris(1,1-dichloroethyl)-s-trioxane were prepared and characterized.

While vapor phase chlorination of aliphatic ketones<sup>1</sup> produces good yields of 2-chloro ketones, application of the same technique to aldehydes results in the production of the corresponding acyl halides.<sup>2</sup> Although the haloform reaction of methyl ketones is well known, the chlorination of aldehydes in an alkaline medium results in both aldol condensation and/or oxidation. With the exception of ethanal, the chlorination of aldehydes in aqueous acid had not been evaluated until Guinot and Tabeteau<sup>3</sup> reported that 2-chlorobutanal and 2-chlorohexanal could be prepared in good yields in the presence of hydrochloric acid at approximately 15°. By raising the temperature to 30° after monochlorination of acetaldehyde was complete, 2,2-dichloroethanal was also prepared in 85% yield. Krattiger<sup>4</sup> refined the method and produced 2-chlorobutanal in 70% yields. However, the application of these procedures to propanal gives 2-chloropropanal (I) in only 35% yield and 2,2-dichloropropanal (II) in less than 10% yield.

In the previously described methods,<sup>3,4</sup> the initial acid concentration was either 2.5*N* or 6–8*N*, and it was allowed to increase freely during the course

of the reaction. The work herein described was carried out under controlled acid concentrations and demonstrates that not only the acid concentration but the acid type determines the reaction products. The results of a series of reactions designed to determine the effects of controlled acid concentration at 10–15° are shown in Table I.

TABLE I  
EFFECTS OF ACID CONCENTRATION ON PRODUCT RATIO

Run No.	Initial Acid Concentration, <i>N</i>	Range of Concentration <sup>a</sup> during Reaction, <i>N</i>	Yield of 2-Chloropropanal, %	Yield of Propionic Acid, %
1	0	0–0.5	0	98
2	3 (HCl)	2.9–3.1	8	90
3	4.5 (HCl)	4.5–4.7	90	<5
4	6 (HCl)	6.1–6.3	92	<5
5	10 (HCl)	10–11	30	0 <sup>b</sup>
6	6 (H <sub>2</sub> SO <sub>4</sub> )	6–6.1 <sup>c</sup>	74	24
7	6 (H <sub>2</sub> SO <sub>4</sub> )	6–6.1 <sup>d</sup>	0	95

<sup>a</sup> Total acid concentration (phenolphthalein end point).

<sup>b</sup> The principal product was a high-boiling neutral material produced by the aldol reaction. <sup>c</sup> 100% conversion of propanal. <sup>d</sup> 20% conversion; one mole aldehyde converted by one mole chlorine.

At low acid concentrations (Runs 1 and 2) oxidation predominated and at high concentrations (Run 5) the product consisted of chlorinated aldol-type

(1) R. Justoni, *Chim. e ind. (Milan)*, 24, 89–94, 195–201 (1942).

(2) R. W. Tess, and G. W. Hearne, U. S. Patent 2,490,386 (1949).

(3) H. Guinot and J. Tabeteau, *Compt. rend.*, 231, 234 (1950).

(4) A. Krattiger, *Bull. soc. chim. France*, 222 (1953).

TABLE II  
 PREPARATION OF 2,2-DICHLOROPROPANAL (II)

Salt Concn., <i>M</i>	Acid Concn., <i>N</i>	Yield of I, %	Yield of II, %	Yield of CH <sub>3</sub> CHCl- CO <sub>2</sub> H, %	Yield of CH <sub>2</sub> CCl <sub>2</sub> - CO <sub>2</sub> H, %	Yield of C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H, %
—	4-4.1	2	50	27	8	12.5
—	6-6.1	2	57	1	6	Trace <sup>a</sup>
—	10-11	4	34	Trace	Trace	Trace <sup>a</sup>
MgCl <sub>2</sub> (3)	4-11	7	10	—	—	10 <sup>a</sup>
MgCl <sub>2</sub> (3)	0-11	17	41	3	8	30

<sup>a</sup> Chlorinated aldols accounted for the remainder.

products. Between total acid concentrations of 4.5*N* and 6.5*N*, the reaction proceeded smoothly to produce I in 90% yields. When hydrochloric acid was replaced by sulfuric acid under nearly identical conditions, the yield of 2-chloropropanal was reduced approximately 20% and that of organic acids equally increased. A partial reaction in sulfuric acid (Run 6) demonstrated that the first mole of chlorine to react produced one mole of propanoic acid. Similar results were obtained in an initially neutral medium when one mole of propanal was converted to one mole of propanoic acid with the simultaneous formation of two moles of hydrogen chloride. It therefore appears that acid alone cannot completely suppress the oxidation reaction in the absence of chloride ions.

It appears that chloride ion may be playing an important role as further evidenced by the fact that chlorination in initially neutral 3*M* solutions of calcium chloride, magnesium chloride, and magnesium sulfate produced I in 67% to 70% yields and propanoic acid in 30% to 32% yields at 100% conversions. At 20% conversion an 18% yield of I was realized in aqueous 3*M* magnesium chloride, but no chloroaldehydes were found when 3*M* magnesium sulfate was used.

The preparation of 2,2-dichloropropanal (II) was carried out as both a one-step and a two-step procedure. The one-step process consisted of completing monochlorination at 10° to 15° and then raising the temperature to 60°, whereupon the second chlorine was introduced. Runs of this type, when taken to completion, usually gave 50% to 60% yields of II and considerable quantities of acids and aldols (Table II). The formation of by-products was essentially eliminated by employing a two-step procedure, wherein hydrated 2-chloropropanal was isolated and added to an equal volume of 10*N* hydrochloric acid. In this medium the chlorination proceeded rapidly at 30-32° and produced II in 87% yield. Under the conditions of the one-step procedure, dichlorination was not detected below 50°.

Although II has been previously reported,<sup>5</sup> this is believed to be the first instance wherein it has been prepared in quantity and properly characterized. The aldehyde (II) was oxidized to 2,2-dichloropropanoic acid in 78% yield and was re-

duced by lithium aluminum hydride to 2,2-dichloropropanol<sup>6</sup> (III). The oxidation of III to 2,2-dichloropropanoic acid completed the proof. Treatment of II with an excess of cold concentrated sulfuric acid afforded a 55% yield of 2,4,6-tris-(1,1-dichloroethyl)-*s*-trioxane<sup>7</sup> (IV), which has a m.p. of 121-121.5°. Spring and Tart<sup>5</sup> reported that II had a m.p. of 111-112° and are therefore assumed to have prepared IV instead of II. A hydrate (V) of II has practically the same properties as those attributed to II by Moelants;<sup>5</sup> however, it was found that I, as well as II, always co-distilled with water at 78° to 80° from solutions of any concentration of water and aldehyde. Compound V had a wide melting point range indicating a relatively unstable hydrate. The pyrolysis of IV produced small quantities of II.

#### EXPERIMENTAL<sup>8</sup>

*2-Chloropropanal* (I). The solution of 2000 ml. of 6.5*N* hydrochloric acid was cooled to and maintained at or below 10° while 580 ml. (8.0 moles) of freshly distilled propanal was added dropwise. Chlorine was introduced below the surface at such a rate as to maintain the temperature between 10° and 15°. At intervals of 15 to 30 min., a 1.0-ml. aliquot was removed from the mixture and titrated with 0.1*N* caustic to a phenolphthalein endpoint. A time interval was so chosen that the acid normality range was approximately 6.0-6.2 or less. The volume of the solution being known, the quantity of water necessary to reduce the total acid concentration of 6.0*N* was calculated and added. When chlorine ceased to be absorbed, the reaction mixture was diluted to 4500 ml. with water and distilled. All material distilling below 68°/185 mm. was collected. Upon redistillation, the fraction boiling below 60°/185 mm. amounted to 830 g.; it proved to be I of 84% purity (+H<sub>2</sub>O 16%). The material was azeotropically dried and distilled; product: b.p. 86°/764 mm.,  $n_D^{20}$  1.4222,  $d_4^{20}$  1.16; reported<sup>9</sup> b.p. 86°,  $n_D^{15}$  1.431,  $d_4^{15}$  1.18.

(5) W. Spring and E. Tart, *Bull. soc. chim.* [3], 3, 402-405 (1890) reported II to be a solid having a m.p. 111-112°; W. Moelants, *Bull. soc. chim. Belg.*, 52, 57 (1943) reported a solid of m.p. 38-39° and b.p. 77-78°/759 mm.; G. A. Razuvaev *et al.*, *J. Gen. Chem. USSR*, 29, 2942 (1959) recently reported a liquid, b.p. 86°, from chlorination of propanol.

(6) This new compound was first prepared by essentially the same method in unpublished work by H. F. Brust, Dow Chemical Co., Midland, Mich.

(7) Unreported in the literature.

(8) All melting points and boiling points are uncorrected.

(9) A. Brochet, *Ann. de chim. et de phys.*, [7] 10, 341 (1897).

*Anal.* Calcd. for  $C_3H_2ClO$ : Cl, 38.38. Found: Cl, 37.99.

*2,2-Dichloropropanal (II) from propanal.* The initial part of this procedure was the same as that for I; however, after monochlorination was completed, the temperature of the solution was gradually raised to 60° and the chlorination continued until chlorine again ceased to be absorbed. The solution was rapidly distilled, and all material boiling 68°/185 mm. was collected as crude II. After redistillation, the material boiling below 60°/185 mm. consisted of 313 g. of II, 11 g. of I, and 54 g. of water. The material was azeotropically dried and distilled b.p. 85°/765 mm. In order to destroy residual I, the product was allowed to stand for 4 hr. over 50 g. of phosphorus pentoxide and then distilled at 180 mm.; product: b.p. 86.0/765 mm.,  $n_D^{20}$  1.4284,  $d_4^{20}$  1.248; chloral-like odor.

*Anal.* Calcd. for  $C_3H_4Cl_2O$ : C, 28.35; 3.15; Cl, 55.85. Found: C, 28.31; H, 3.08; Cl, 55.80.

The aqueous acid solution remaining after distillation of the crude aldehyde was subjected to continuous ether extraction for 24 hr. Drying and distillation gave 9.6 g. of propanoic acid, 146 g. of 2-chloropropanoic acid, and 61 g. of 2,2-dichloropropanoic acid.

*2,2-Dichloropropanal (II) from 2-chloropropanal (I).* To 250 g. of 84% I cooled to 5° was added, dropwise, 180 ml. of cold 10N hydrochloric acid. The introduction of chlorine was started and the temperature was slowly increased to about 30°. When chlorine consumption ceased, the mixture was diluted with 1 l. of cold water. The crude aldehyde was separated by distillation, all material boiling below 65°/185 mm. being collected. After drying the crude distillate: 253 g. of 99.8% II, b.p. 86°, was collected on redistillation.

The characteristic peak in the infrared spectrum of II which was frequently used for analytical purposes was 7.28 (m).

Vapor phase chromatographic analysis was carried out on a 3-ft.  $\times$  1/4-in. column of 30% TCP on Celite at room temperature and 15 p.s.i.g. of helium.

*Drying of chlorinated aldehydes.* (A) To a 200-ml. flask equipped with a Dean-Stark trap were added 500 ml. each of ethyl ether and aldehyde-water mixture (crude product), and 250 ml. of xylene. The mixture was brought to reflux and additional xylene added dropwise until water was observed to form a heterogeneous azeotrope with the ether; this usually occurred when the liquid temperature reached approximately 65° to 70°. This temperature range is probably required in order to effect the decomposition of the aldehyde hydrate into free aldehyde and water.

Ether alone will not remove the water, while benzene and carbon tetrachloride have boiling points which make the separation from the aldehyde by distillation very difficult. By employing a high-boiling material such as xylene to increase the liquid boiling temperature and ether to azeotrope with the water, these problems were overcome.

(B) *Molecular sieves.* Equal volumes of xylene, aldehyde-water mixture, and 5A sieves were mixed and warmed to

70° for 4 hr. in a protected flask. Cooling, filtration, and distillation produced a product containing less than 1% water.

*2,2-Dichloropropanol (III) from 2,2-dichloropropanal (II).* To 500 ml. of dry ether cooled in an ice-salt bath was added 9.5 g. of lithium aluminum hydride followed by 127 g. of II, dropwise. The mixture was allowed to warm to 25° and was stirred for an additional 2 hr. After cooling to 0°, 35 ml. of water was added and then 200 ml. of 15% aqueous sulfuric acid. The ether layer was removed and the aqueous phase washed with two 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and sodium bicarbonate, and distilled; 79 g. of III, b.p. 80°/90 mm.,  $n_D^{20}$  1.4661,  $d_4^{20}$  1.31.

*Anal.* Calcd. for  $C_3H_6Cl_2O$ : C, 27.90; H, 4.64; Cl, 55.03. Found: C, 27.79; H, 4.60; Cl, 54.80.

*Oxidation of II to 2,2-dichloropropionic acid.* To 39.6 g. of potassium permanganate dissolved in 100 ml. of 1% sodium hydroxide was added 23.5 g. of II. After standing overnight, the mixture was acidified with 6N sulfuric acid and sodium sulfite was added until the solution cleared. Extraction with ether, drying, and distillation gave 21.5 g. of 2,2-dichloropropionic acid, b.p. 50–55°/0.1 mm.

*Anal.* Calcd.: Neut. equiv., 143. Found: Neut. equiv., 142.

The infrared spectrum of the acid was identical with that of an authentic sample.

*Oxidation of 2,2-dichloropropanol (III) to 2,2-dichloropropionic acid.* Twenty-six grams of III was oxidized in the same manner as II; 20.8 g. of the same acid was isolated.

*Preparation of 2,4,6-tris(1,1-dichloroethyl)-s-trioxane (IV).* One hundred grams of II was added with stirring to 500 ml. of cold concd. sulfuric acid. After 3 hr., the aldehyde separated into an upper layer and slowly solidified. The solid was removed, washed with water, and recrystallized from petroleum ether (b.p. 32–45°); 61 g. of IV, m.p. 121–121.5°.

*Anal.* Calcd. for  $C_9H_{12}Cl_6O_3$ : C, 28.35; H, 3.15; Cl, 55.85; mol. wt., 381. Found: C, 28.27; H, 3.11; Cl, 55.51; mol. wt., 376.

Pyrolysis of 10 g. of IV produced 2.6 g. of II and considerable tar and hydrogen chloride.

*Preparation of 2,2-dichloropropanal hydrate (V).* One hundred twenty-seven grams of I was mixed with 18 g. of water and cooled to 10° for 24 hr. A white solid formed; product: Softens 35–40°, m.p. 47–53°; b.p. 79–80°, distillate is initially two phases, water/II, which slowly solidified with evolution of heat to form V.

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